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## CLAIMS

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[Claim(s)]

[Claim 1] The rechargeable battery characterized by being the rechargeable battery which makes a basic component the positive electrode which makes a lithium inclusion compound metallic oxide a positive active material, the negative electrode which makes a carbonaceous material a negative-electrode active material, a separator, the organic electrolytic solution, and a cell container, and the moisture content contained in this organic electrolytic solution being 5 ppm - 450 ppm.

[Claim 2] The rechargeable battery according to claim 1 characterized by coming to prepare one [ at least ] electrode an active material coat on the metal current collection field, and distributing the binder in this active material coat by the binder distribution factors 0.5-5.0.

[Claim 3] The rechargeable battery according to claim 2 characterized by for the metal current collection field being a metallic foil, and the surface roughness of this metallic foil being 0.1 micrometers - 0.9 micrometers.

[Claim 4] The rechargeable battery according to claim 2 characterized by making into a principal component the styrene / butadiene latex a binder is 40 % of the weight - 95 % of the weight of butadiene contents, and is [ latex ] 75% - 100% of gel contents.

[Claim 5] The rechargeable battery according to claim 1 characterized by the thing for which the organic electrolytic solution was chosen out of ether, ketones, lactone, nitril, an amines, amides, a sulfur compound, chlorinated hydrocarbons, ester, carbonate, the nitro compound, the phosphoric ester system compound, and the sulfo run system compound, and which makes a kind a solvent at least.

[Claim 6] The rechargeable battery according to claim 1 characterized by this negative electrode occupying both the most inner circumference and the outermost periphery in the cell structure which carries out separator \*\*, carries out opposite arrangement of the positive/negative electrode, and comes to involve it in.

[Claim 7] The rechargeable battery according to claim 1 characterized by equipping with PTC element whose induction temperature coefficient operation temperature is 80 degrees C - 140 degrees C, and is - 10--130 as a safety device.

[Claim 8] Operation of the rechargeable battery characterized by making the pocket electronic equipment which consists of an IC element which operates by 3.5V-2.6V drive in the rechargeable battery single cell whose moisture content contained in this organic electrolytic solution it is the rechargeable battery which makes a basic component the positive electrode which makes a lithium inclusion compound metallic oxide a positive active material, the negative electrode which makes a carbonaceous material a negative-electrode active material, a separator, the organic electrolytic solution, and a cell container, and is 5 ppm - 450 ppm.

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[Translation done.]

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] this invention relates to the new rechargeable battery excellent in cycle nature, a store property, and safety.

[0002]

[Description of the Prior Art] In recent years, various non-drainage-system rechargeable batteries are proposed as small [ which changes to the conventional acid-lead cell, and nickel/cadmium cell ], and a lightweight rechargeable battery. The new rechargeable battery system which uses a carbonaceous material for a negative electrode especially using the compound metallic oxide which makes Li and Co a principal component in the positive electrode currently indicated, for example in JP,62-90,A, a No. 863 official report, JP,63-121,A, a No. 260 official report, JP,3-49,A, the No. 155 official report, etc. attracts attention.

[0003] What uses the metal Li or Li alloy was conventionally proposed as a negative-electrode active material as such a non-drainage-system rechargeable battery. from small and the viewpoint of being lightweight, although the rechargeable battery which used such a metal Li etc. for the negative electrode was satisfied, since performance problems, such as cycle nature, a store property, etc. based on a dendrite precipitation, and the separator by dendrite precipitation similarly broke it through, it had a serious failure to utilization, such as a problem of the life of causing the internal shunt, and a problem when [ safe ] based on a still activity metal [ Li ] chemical reactivity

[0004] On the other hand, since the new fuel cell subsystem which uses a carbonaceous material for the aforementioned negative-electrode active material does not have an activity chemical reactivity like a metal Li while it has the outstanding cycle nature and the outstanding store property, without causing such a dendrite precipitation, it has the characteristic feature that safety is very excellent.

[0005] When it combines with Li inclusion compound metallic oxide as a positive active material especially, it is expected as what can do the cell of the high voltage and high capacity.

[0006]

[Problem(s) to be Solved by the Invention] By the way, such a Li inclusion compound metallic oxide is made into a positive active material, and the performance of a cell and safety are greatly influenced by the moisture content contained in the electrolytic solution to use in the nonaqueous electrolyte cell using the carbonaceous material as a negative-electrode active material. For example, when many moisture contains in the electrolytic solution in remainder, while the bad influence on the performance of a fall of current efficiency and a fall of cycle nature comes out, the phenomenon which becomes the safe upper problem of a gassing and internal pressure elevation by the reaction with moisture occurs.

[0007] However, although it is theoretically possible to make the moisture content in the electrolytic solution about into zero when the manufacturing process of an actual cell is considered, it becomes high in cost extremely. When using especially the carbonaceous material of this invention for a negative-electrode active material, the moisture content permitted differs from the case where the conventional metal Li is used as a negative-electrode active material. Therefore, it is an important technical problem

to clarify the moisture content permitted in the fuel cell subsystem of this invention, and to find out the balance domain of practicality.

[0008]

[Means for Solving the Problem and its Function] As a result of considering zealously the influence by the moisture content of this fuel cell subsystem, this invention person etc. maintained the property which was excellent in the specific moisture-content domain, and found out that safety was also secured.

[0009] The rechargeable battery of this invention is a rechargeable battery which makes a basic component the positive electrode which was completed based on such knowledge and makes a lithium inclusion compound metallic oxide a positive active material, the negative electrode which makes a carbonaceous material a negative-electrode active material, a separator, the organic electrolytic solution, and a cell container, and the moisture content contained in this organic electrolytic solution is characterized by being 5 ppm - 450 ppm.

[0010] In this invention, especially the inclusion moisture content must be important and the domain of it must be 5 ppm - 450 ppm. It is the domain of 15 ppm - 300 ppm preferably.

[0011] In exceeding 450 ppm, while gas, such as hydrogen gas, occurs at the time of initial charge and internal pressure rises, phenomena, such as blistering of a cell, generate and are not desirable. Moreover, in order to control to a less than 5 ppm moisture content, while very prolonged dehydration processing is required like the above-mentioned, it is not set as an erector and moisture needed [ very advanced ], and desirable.

[0012] In order to control a moisture content in the domain of this invention, about the electrolytic solution, the method of using dehydrating agents, such as a molecular sieves, etc. is adopted. Moreover, about member moisture, such as positive, a negative electrode, and a separator, each may be dried preparatorily, and technique, such as establishing a xeransis process, is adopted before electrolytic-solution sinking in as a cell erector.

[0013] Moreover, since the activity matter is not used to the moisture of a metal lithium etc., especially advanced dry conditions are not so required as the erector for positive [ of the combination of this invention ], and a negative electrode. When establishing a xeransis process especially before electrolytic-solution sinking in, even if it performs the process till then in the usual atmospheric air, it can be controlled to the moisture content of the limited domain of this invention.

[0014] Like the above, in the case of the cell of positive [ of this invention ], and the combination of a negative electrode, the moisture content of a large domain is permitted compared with the conventional lithium cell etc., and it becomes a practically big advantage.

[0015] Li compound metallic oxide said by this invention is a compound which has the layer structure, and Li ion intercalates and can deintercalate electrochemically. General formula  $\text{Li}_x\text{Co}_y\text{N}_z\text{O}_2$  (however) currently indicated in  $\text{LiCoO}_2$  indicated, for example in JP,55-136,A and a No. 131 official report, JP,62-90,A, and the No. 863 official report if an example of such a compound metallic oxide is shown, although not limited especially N was chosen out of the group of aluminum, In, and Sn -- a kind is expressed at least and x, y, and z express the number of each  $0.05 \leq x \leq 1.10$ ,  $0.85 \leq y \leq 1.00$ , and  $0.001 \leq z \leq 0.10$  moreover,  $\text{Li}_x\text{Ni}_y\text{Co}_{(1-y)}\text{O}_2$  (however,  $0 < x \leq 1$ ,  $0 \leq y < 0.50$ ) indicated in JP,3-49,A and a No. 155 official report -- further --  $\text{Li}_x\text{MnO}_2$  etc. -- it is mentioned

[0016] In order to obtain such a compound, if it requires further, it will be easily obtained by the baking reaction with other metallic compounds with Li compounds, such as a lithium hydroxide, a lithium oxide, a lithium carbonate, and a lithium nitrate, a metallic oxide and a metal hydroxide, a metal carbonate, a metal nitrate, etc.

[0017] These multiple oxides have the outstanding property which is not seen also for what \*\* in other active materials called the high voltage and high capacity as a positive active material. especially aforementioned general formula  $\text{Li}_x\text{Co}_y\text{N}_z\text{O}$  [ especially ]2 (however, N was chosen out of the group of aluminum, In, and Sn -- a kind is expressed at least and x, y, and z express the number of each  $0.05 \leq x \leq 1.10$ ,  $0.85 \leq y \leq 1.00$ , and  $0.001 \leq z \leq 0.10$ ) is a multiple oxide which is excellent in properties, such as cycle nature, and is preferably used by this invention

[0018] Moreover, although especially the carbonaceous material said by this invention is not limited, if

it shows the example, the baking carbide of the condensation polycyclic hydrocarbon system compound of a publication etc. will be mentioned to baking carbide, such as a phenol system resin given in JP,58-35,A, a high surface-area carbon material given in a No. 881 official report, graphite and JP,58-209,A, and a No. 864 official report, and JP,61-111,A, and a No. 907 official report. The carbonaceous material which has BET adsorption method specific-surface-area A (m<sup>2</sup> / g) indicated in JP,62-90,A and a No. 863 official report especially in the domain in which the value of the crystal thickness Lc (\*\*) and true-density rho (g/cm<sup>3</sup>) in X-ray diffraction fills following condition 1.70<rho<2.18 and 10<Lc<120rho-189 in 0.1<A<100 has high capacity and the outstanding cycle property, and is especially used preferably in this invention.

[0019] Although it is not limited, after especially the molding technique of the electrode using such an active material distributes an electrode active material in the solvent solution of an organic polymer, the coating method which carries out coating xeransis can attain a thin film and large area-ization, and it is desirable. [ of a method ] In this case, that come to prepare one [ at least ] electrode an active material coat on the metal current collection field, and the binder in this active material coat is distributed by the binder distribution factors 0.5-5.0 prevents a fall of a paint film intensity, the poor contact between active material grain, etc., it can improve the elevated-temperature property of the rechargeable battery of this invention, and it is desirable. a binder distribution factor -- desirable -- 0.75-2.5 -- it is 0.75-2.0 more preferably

[0020] The binder distribution factor said here is a coefficient defined by the below-mentioned measuring method, and the ratio with the amount of binders which exists in a 10-micrometer layer thickness from the amount of binders which exists in a 10-micrometer layer thickness from an active material layer front face, and a current collection field side active material layer interface is expressed.

[0021] A <measurement of binder distribution factor> sample:electrode is hardened by the epoxy resin, and let what carried out the disconnection polishing of the electrode cross section be a sample.

[0022] Measurement: Measure the amount of binders in the active material of an electrode cross section by EPMA (electron microprobe analysis method).

[0023] Equipment is HITACHI. X-650 (Hitachi make)

HORIBA EMAX-2200 (Horiba make)

Wavelength-dispersion type EPMA is used.

[0024] A lower formula performs <calculation of binder distribution factor> binder distribution factor.

[0025]

[Equation 1]

$$\text{バインダー分布係数} = \frac{\text{活物質層表面から } 10 \mu \text{ までの層のバインダー量}}{\text{集電体側活物質界面から } 10 \mu \text{ までの層のバインダー量}}$$

In addition, pretreatments, such as dyeing for the above-mentioned measurement, are arbitrarily chosen according to the modality of binder.

[0026] When the distribution factor of a binder is less than 0.5, the intensity on the front face of a paint film is weak, and absence of an active material etc. generates and is not desirable. Moreover, when a binder distribution factor exceeds 5.0, cell performances, such as a cell property especially cycle nature, a store property, and output characteristics, get worse and are not desirable.

[0027] In order to set a binder distribution factor to 0.5-5.0, it is attained by optimizing the conditioning in the describing [ above ] coating method. As a condition factor at that time, selection of a binder, selection of a coating liquid solvent, coating liquid viscosity, coating liquid solid concentration, the xeransis technique, drying temperature, etc. are mentioned.

[0028] Although not limited especially, generally the direction [ a rate of drying is slow ] gives the result with the higher one desirable [ coating liquid viscosity and solid-content concentration ].

[0029] Although not limited especially as metal current collection field used for an electrode, since that

the metal current collection field is a metallic foil, and the surface roughness of this metallic foil is 0.1 micrometers - 0.9 micrometers strengthens the adhesive property of an active material and a metallic foil and it can improve an elevated-temperature property too, it is desirable.

[0030] The appearance of this metallic foil presents grinding. 0.2-0.8-micrometer 0.1-0.9 micrometers are preferably controlled by etching processing, the lasing, electroless deposition, electrolysis plating, the blast cleaning, etc. still preferably as a surface roughness to the aforementioned metallic foil which has the appearance of gloss and semigloss at 0.6-0.8 micrometers. Moreover, you may use what goes into the above-mentioned surface-roughness domain in the copper foil directly obtained by electrolysis plating, a nickel foil, etc.

[0031] Hardly, there is adhesive enhancement, and if no exceeds 0.9 micrometers, it causes [ into a coating ] a disconnection of a metallic foil and is desirable at less than 0.1 micrometers of surface roughness.

[0032] 30-300 micrometers of the thicknesss of the positive active material and binder which have been pasted up on the metallic foil are 70-130 micrometers more preferably per one side. As a metallic foil used for a positive electrode, aluminum with a thickness of 100-5 micrometers, nickel, a stainless steel, etc. can be used. It is aluminum preferably and a 30-10-micrometer thing is used still preferably the thickness of 50-8 micrometers.

[0033] Moreover, 60-750 micrometers of the thicknesss of the negative-electrode active material and binder which have been pasted up on the metallic foil are 140-400 micrometers more preferably per one side. As a metallic foil used for a negative electrode, copper with a thickness of 100-5 micrometers, nickel, a stainless steel, etc. can be used. It is copper and a stainless steel preferably and a 25-8-micrometer thing is used still preferably the thickness of 50-6 micrometers.

[0034] Manufacture of the test piece for measuring a surface roughness is first started on 1cm square from a metallic foil, puts this into a mold, and slushes and stiffens an epoxy resin. In ordinary temperature, it takes out from a mold, and cuts after the neglect between days, the resin cut surface containing a metallic foil is ground with the grinder which rotates and revolves around the sun, and the microphotography of a cross section is taken after an air blow. The depth of the concavity on the front face of a metallic foil is measured with an enlargement, and let an average depth be a surface roughness.

[0035] The adhesive test of active material grain and a metallic foil is cut out by the width of face of 2cm to a metallic foil from an application or the electrode by which carries out a coating, dries, and carries out a compression press, and sizing was carried out, and cuts out active material grain and a binder by NT cutter in length of 5cm. Let this be a test sample.

[0036] The 2cm fraction is exfoliated from the edge in the length orientation of the piece of decision in the active material and binder which were pasted up, a metallic foil front face is taken out, and this fraction is stopped and hung with a stapler to a metal plate.

[0037] Next, methanol 80ml is put into a 100ml glass beaker. The above-mentioned glass beaker is put into an ultrasonic washer [a model (Yamato 2200)], city water is added between a scrubber container and a glass beaker, and the water surface is made to come upwards from a methanol oil level for a while.

[0038] It is made to sink in the aforementioned test sample completely [ 3cm of active material grain jointings ] in a methanol, and a metal plate is hung with yarn. The start button of an ultrasonic washer is pushed, a ultrasonic wave is generated, and a paint film front face is observed. It observes whether with time progress, a blister is produced from a start on an adhesion cortex.

[0039] Especially as a binder which makes an active material bind to the current collection field, although not limited, various organic polymers are usually used. If an example of such a binder is shown, a poly-fluoride vinyl, a polyvinylidene fluoride, a fluororubber, a polyacrylonitrile, poly-meta \*\*\*\*\* tolyl, a nitrile rubber, ethylene-propylene rubber, a styrene butadiene rubber, a polymethylmethacrylate, a polysulfide rubber, a cyanoethyl cellulose, a methyl cellulose, etc. will be mentioned.

[0040] It faces, using such an organic polymer as a binder. The technique using the thing which made

the binder solution made to melt this organic polymer in a solvent distribute an electrode active material as coating liquid, The technique using the thing which made the water emulsification variance liquid of this organic polymer distribute an electrode active material as coating liquid, the technique of applying the solution and/or distributed liquid of this organic polymer to the electrode active material by which preforming was carried out beforehand, etc. are mentioned as an example.

[0041] although especially the amount of binders to use is not what is limited -- usually -- the electrode active material 100 weight section -- receiving -- 0.1 - 20 weight section -- it is the domain of 0.5 - 10 weight section preferably

[0042] Making into a principal component the styrene / butadiene latex a binder is 40 % of the weight - 95 % of the weight of butadiene contents, and is [ latex ] 75% - 100% of gel contents especially can improve an elevated-temperature property, and it is desirable.

[0043] The gel content of the polymer which this styrene / butadiene latex are industrially manufactured by the usual emulsion-polymerization method, and a butadiene content is 40 % of the weight - 95 % of the weight, makes dry this styrene / butadiene latex further, and is obtained is 90% - 100% preferably 75% to 100%. Here, a gel content means the insoluble matter of the polymer to toluene.

[0044] When a butadiene content is less than 40 % of the weight, the bond strength and flexibility of an electrode are missing. Moreover, a bond strength is missing when 95 % of the weight is exceeded.

[0045] When a gel content is less than 75%, while the bloating tendency-proof to the electrolytic solution used for the bond strength and the non-drainage-system cell mentioned later of an electrode is missing, the charge shelf-life ability under a high temperature service falls.

[0046] although it is not certain why the gel content of styrene / butadiene latex polymer affects elevated-temperature shelf-life ability -- bridge formation of a latex polymer -- it is imagined as that to which the polymer which a degree, i.e., a gel content, affects it and seldom carries out a flow to the flow of the polymer under an elevated temperature suppresses a fall of the electric discharge capacity after an elevated-temperature store

[0047] Moreover, the monomer in which the copolymerization of those other than styrene and a butadiene is possible can be used for styrene / butadiene latex, for example, methyl (meta) acrylate, ethyl (meta) acrylate, butyl (meta) acrylate, acrylonitrile (meta), the ethylene nature unsaturation carboxylate of a hydroxyethyl (meta) acrylate grade, and the ethylene nature unsaturated carboxylic acid that are an acrylic acid, a methacrylic acid, an itaconic acid, a fumaric acid, a maleic acid, etc. further can be used. It is desirable to use dicarboxylic acids, such as an itaconic acid, a fumaric acid, and a maleic acid, especially as an ethylene nature unsaturated carboxylic acid in respect of the bond strength of an electrode. General technique, such as adjustment of polymerization temperature, adjustment of the amount of polymerization initiators, and adjustment of the amount of chain transfer agents, is used for adjustment of a gel content.

[0048] Although it does not limit especially, 0.01-0.5 micrometers of the particle diameters of this styrene / butadiene latex are 0.01-0.3 micrometers more preferably.

[0049] although especially the loadings of this latex are not what is limited -- usually -- the active material 100 weight section -- receiving -- 0.1 - 20 weight section -- it is 0.5 - 10 weight section preferably

[0050] Adhesive power good in under 0.1 weight section is not obtained, but if 20 weight section is exceeded, an overvoltage will go up remarkably, and it is \*\*\*\*\* about a bad influence to a cell property.

[0051] Moreover, although especially the solid-content concentration of coating liquid is not limited, it is usually 40 % of the weight - 65 % of the weight preferably 30 % of the weight to 65% of the weight.

[0052] Furthermore, \*\*\*\* for 2 - 60 weight sections is also good to styrene / butadiene latex solid-content 100 weight section in a water-soluble thickener as an additive.

[0053] As a water-soluble thickener, a carboxymethyl cellulose, a methyl cellulose, a hydroxymethyl cellulose, an ethyl cellulose, polyvinyl alcohol, a polyacrylic acid (salt), oxidization starch, phosphorization starch, casein, etc. are contained.

[0054] Moreover, a component except a water-soluble thickener is not eliminated an active material,

styrene / butadiene latex, and if needed. For example, dispersants, such as sodium hexametaphosphate, the Tripoli sodium phosphate, pyrophosphoric-acid soda, and a sodium polyacrylate, and the thing which added additives, such as the Nonion nature as a stabilizing agent of a latex and an anionic surfactant, further are also contained. the mean particle diameter of the carbonaceous material which is a negative-electrode active material when using styrene / butadiene latex -- a fall of current efficiency, and a fall of the stability of a slurry -- \*\*\*\* -- having -- it is preferably more suitable than problems, such as increase of the resistance between grain within the paint film of an electrode, that it is [ 0.1-50-micrometer / 3-25-micrometer ] the domain of 5-15 micrometers still preferably

[0055] The application xeransis of the slurry is carried out on a base material as coating liquid, and an electrode is fabricated. If it requires at this time, you may fabricate with a current collection field material, and the current collection fields, such as aluminum foil and copper foil, can also be used as a base material as another law.

[0056] Moreover, as such a method of application, arbitrary coating-machine heads, such as the reverse-video rolling method, the comma bar method, the \*\*\*\*\* method, and the air knife method, can be used.

[0057] Although not limited especially as a separator, although textile fabrics, a nonwoven fabric, a glass cloth, a synthetic-resin fine porosity layer, etc. are mentioned, when using a thin film and a large area electrode, the synthetic-resin fine porosity layer indicated by JP,58-59072,A, especially a polyolefine system fine porosity layer are desirable in respect of thickness, an intensity, and a membrane resistance.

[0058] Although not limited especially as an electrolyte of nonaqueous electrolyte, if an example is shown LiClO<sub>4</sub>, LiBF<sub>4</sub>, LiAsF<sub>6</sub>, and CF<sub>3</sub> SO<sub>3</sub> Li, 2 (CF<sub>3</sub> SO<sub>2</sub>) N, Li and LiPF<sub>6</sub>, LiI, LiAlCl<sub>4</sub>, NaClO<sub>4</sub>, NaBF<sub>4</sub>, NaI, 4 (n-Bu) N+ClO<sub>4</sub>, 4 (n-Bu) N+BF<sub>4</sub>, and KPF<sub>6</sub> A grade is mentioned.

[0059] As an organic solvent of the electrolytic solution used, although ether, ketones, lactone, nitril, an amines, amides, a sulfur compound, chlorinated hydrocarbons, ester, carbonate, a nitro compound, a phosphoric ester system compound, a sulfo run system compound, etc. can be used, for example, ether, ketones, nitril, chlorinated hydrocarbons, carbonate, and a sulfo run system compound are desirable also among these. Furthermore, it is annular carbonate preferably. As these examples of representation, a tetrahydrofuran, 2-methyl tetrahydrofuran, 1, 4-dioxane, an anisole, a mono-glyme, an acetonitrile, A propionitrile, a 4-methyl-2-pentanone, a butyronitrile, Valeronitrile, a benzonitrile, 1, 2-dichloroethane, gamma-butyrolactone, Dimethoxyethane, a methyl \*\*\*\*\* mate, propylene carbonate, Although ethylene carbonate, vinylene carbonate, a dimethylformamide, dimethyl sulfoxide, a dimethyl thio formamide, a sulfo run, a 3-methyl-sulfo run, trimethyl phosphate, phosphoric-acid triethyl, these mixed solvents, etc. can be raised It is not necessarily limited to these.

[0060] Furthermore, if it requires, a cell is constituted using parts, such as the current collection field, a terminal, and an electric insulating plate.

[0061] Although the gestalt of the cylinder-like cell around which the paper type cell which is not limited and used the positive electrode, the negative electrode, and the separator as the monolayer or the double layer especially as structure of a cell, the laminating type cell or the positive electrode, the negative electrode, and the separator were wound in the shape of a roll is mentioned as an example If it is the cell structure where carry out separator \*\*, carry out opposite arrangement of the positive/negative electrode, come to involve it in, and a negative electrode occupies both the most inner circumference and the outermost periphery, since the amount of the metal lithium to separate can be decreased remarkably The degradation by a fall of the cell capacity by repeat use, self-discharge, and the surcharge can be prevented, and it is desirable.

[0062] In such structure, it is the point that the section and the end section of a volume are wearing a positive-active-material side completely by the negative electrode through a separator at electrode volume the beginning of the winding field, and a positive active material is made to be not exposed. Although the negative electrode used at this time made only one side of the metallic foil current collection field install an active material, even if what doubles a metallic foil side and becomes in piles may be used for it and the thing which made both sides of a metallic foil install an active material



uniformly is used for it, it is not cared about. Also in the positive electrode, it is the same.

[0063] Although the shorter one is good when the length with a negative electrode excessive seen from a positive electrode considers the amount of stuffings for a positive-active-material side a wrap case completely by the negative electrode through a separator, when a too short design is carried out, there is a possibility that the winding field which a positive active material exposes may be made according to factors, such as thickness dispersion of each electrode and the electrode length measurement precision of take-up motion. Therefore, the distance between each edge of positive [ which it \*\*\*\*s, and a positive electrode is completely covered by the negative electrode through a separator in a fraction and the end fraction of a volume, and counters through a separator in the aforementioned site ], and a negative electrode is in the winding field status, and it is desirable to be referred to as 1-10nm. Furthermore, it is good to be preferably referred to as 2-5nm.

[0064] It is desirable to equip the rechargeable battery of this invention with PTC element whose induction temperature coefficient operation temperature is 140 degrees C - 80 degrees C, and is -10--130 as a safety device.

[0065] As a PTC element, it is BaTiO<sub>3</sub>. Although various things are known from the former, such as a ceramic system, PTC elements which this invention defines are an overcurrent by the conductive polymer with PTC property (property that resistance becomes large as temperature goes up), and an overheat-protection element. For example, what is marketed from Raychem as various protection elements in the tradename of Polyswitch (registered trademark) poly switch is mentioned. When this element induces both temperature and a current and a fixed upper limit is exceeded, it has the function which element resistance goes up automatically and intercepts a current. It is already well-known to equip a cell with such a PTC element. For example, by equipping a lithium primary cell, when a cell short-circuits via an external circuit, this PTC element operates, a current is intercepted, and practical use is already presented with securing the safety of a cell.

[0066] The following fact became clear as a result of this invention person's etc. examining the overcharge process of the rechargeable battery of this invention in detail.

[0067] \*\*. By the time it results in rupture at the time of overcharge, generation of heat should surely follow.

[0068] \*\*. Carry out proportionality dependence of the temperature rise of the cell by this generation of heat at the overcharge current.

[0069] \*\*. Correlate the cell can temperature at the time of rupture with the overcharge current, and the cell can temperature surveyed at the time of rupture should become low so that a overcharge current is large. (Since a temperature rise speed is large, temperature distribution occur, and this is imagined to be what the value lower than the temperature in an actual cell can is detected as.)

It is not more effective than the above fact to equip with the thermal fuse which responds only at temperature as a means to secure the safety at the time of overcharge of the rechargeable battery of this invention.

[0070] Moreover, when it equips with the current fuse which similarly responds only with a current, the current precision which can respond is bad, the distinction with a normal current and a overcharge current is impossible, and it is not the same effective means.

[0071] Therefore, the behavior at the time of overcharge of the rechargeable battery of this invention differs from the behavior of other cells greatly, and this is considered to be the behavior based on the combination of the active material of positive and negative two electrodes used by the rechargeable battery of this invention. therefore -- in order to secure the safety at the time of overcharge of the rechargeable battery of this invention -- both temperature and a current -- responding -- a value negative in the induction temperature coefficient -- it is -- in addition -- and it is required to have the induction temperature coefficient of a fixed domain An induction temperature coefficient here is a parameter which is measured by the below-mentioned measuring method and shows the current dependency of induction temperature.

[0072] A <measurement of induction temperature coefficient> PTC element is connected to constant-current DC power supply, and the temperature up is carried out within oven, energizing a fixed current



(A). The temperature (\*\*) at the time of the resistance of PTC element increasing 1000 times at the time of a room temperature is measured. A current value is changed, the again same operation is performed, and a total of five points is measured. Temperature is plotted on a quadrature axis and the measured value of five points is plotted for a current value on an axis of ordinate. Let this slope of a line be an induction temperature coefficient.

[0073] The operation temperature said by this invention means temperature in case resistance reaches 1000 times at the time of a room temperature only at temperature, when a current value is a zero.

[0074] The operation temperature of PTC element used by this invention must be 80 degrees C - 140 degrees C. It is 85 degrees C - 140 degrees C preferably. In exceeding 140 degrees C, even if it compares and PTC element operates at the temperature, generation of heat continues as it is, it results in rupture, the probability of the incorrect operation by the practical use operating temperature limits becomes high at less than 80 degrees C, and it is not desirable.

[0075] Moreover, an induction temperature coefficient must be -10--130. desirable -15--100 -- it is -25--80 still preferably

[0076] When an induction temperature coefficient is less than -ten, the case where the prevention to the surcharge in the field where a current value is large becomes not perfect, and explodes is generated. Moreover, in exceeding -130, the current value which can be energized a practical use field, i.e., near a room temperature, becomes small, and becomes practically unusable.

[0077] Although especially the method of equipping a cell with PTC element of this invention is not limited, it is desirable for the technique of equipping, for example in a cell can, the technique of equipping a cell can free wheel plate, the technique of equipping cell \*\*\*\*, etc. to be mentioned, and to equip the part which can detect the temperature of a cell to accuracy more with a natural thing.

[0078] By equipping with PTC element which has the property of the above-mentioned domain, the safety to a surcharge is secured in all current domains, and it is desirable.

[0079] In this invention, especially the moisture content in a cell can is important like the above. A moisture content here is a moisture content in the nonaqueous electrolyte in the status in the cell after assembly that it does not charge. For the following ground, such moisture is usually mixed.

[0080] Although especially the operation of the rechargeable battery of the moisture this invention which mixes in inside the moisture (c). cell erector who contained in the cells member, such as a moisture (b). positive electrode contained in (b). nonaqueous electrolyte, a negative electrode, and a separator, by the atmospheric air etc. is not limited The rechargeable battery of this invention has the high voltage of a single cell, since it can moreover obtain a high-energy density, it is a single cell and the operation of making the pocket electronic equipment which consists of an IC element which operates by 3.5V-2.6V drive of it becomes possible. When the rechargeable battery of this invention is used by such operation, small lightweight-ization of pocket electronic equipment can be attained.

[0081] This pocket electronic equipment can be driven by 4.2V-2.5V, and 4 or less W of power consumption is about [ 3W-0.5W ] preferably. For example, there are a personal computer of 3.3V drive, an one apparatus video camera of 3.5V drive, a mobile transmitter of 3.3V drive, etc.

[0082] In this case, as capacity of the rechargeable battery to use, 400 or more mAhs, it is 1500 or more mAhs and 700 or more mAhs are 4000 or less mAhs still preferably preferably.

[0083] In 400 or less mAhs, if prolonged continuous duty is not borne and 4000mAhs are exceeded, it will become difficult to achieve the purpose of lightweight-izing.

[0084]

[Example] Hereafter, an example explains this invention still in detail.

[0085] Example 1Li1.03Co0.92Sn0.02O2 After mixing Li and the Co multiple-oxide 100 weight section which have composition, the graphite 2.5 weight section, and the acetylene black 2.5 weight section, the liquid made to melt the fluororubber 2 weight section in the 1:1 (weight ratio) partially-aromatic-solvent 60 weight section of ethyl acetate/ethylcellosolve was mixed, and slurry-like coating liquid was obtained.

[0086] The above-mentioned coating liquid was applied to both sides of with a width thickness [ 15micro thickness of 600mm ] aluminum foil using the coater which has a doctor blade coating-

machine head. \*\*\*\*\* after a double-sided coating was 290micro.

[0087] The liquid made to melt the needle-coke trituration article 100 weight section and the fluororubber 5 weight section in the 1:1 (weight ratio) partially-aromatic-solvent 90 weight section of ethyl acetate/ethylcellosolve was mixed, and slurry-like coating liquid was obtained.

[0088] The above-mentioned coating liquid was applied to both sides of with a width thickness [ 10micro thickness of 600mm ] Cu foil using the coater which has a doctor blade coating-machine head. \*\*\*\*\* after a double-sided coating was 350micro.

[0089] Both did the slit of the two aforementioned kinds of coating articles to 41mm width after the press in the calendering roll using the slitter.  $\text{Li1.03Co0.92Sn0.02O2}$  The coating article was made into the positive electrode, the needle-coke coating article was used as the negative electrode, and it wound with an outer diameter of 14.9mm in the shape of a coil with the winding machine, using the fine porosity layer (high pore 4030U Asahi Chemical Industry Co., Ltd. make) made from polyethylene as a separator. It is  $\text{LiBF}_4$  to the partially aromatic solvent of 1:1:2 (weight ratio) of propylene carbonate after putting this winding coil into a cell can with an outer diameter of 16mm / ethylene carbonate / gamma-butyrolactone. What was melted to 1 M concentration was obturated after sinking in as electrolytic solution, and the cell can of A size with a height [ which is shown in drawing 1 ] of 50mm was made as an experiment.

[0090] In addition, - terms and conditions, such as a moisture content of the cell assembly ambient atmosphere at that time and the electrolytic solution, were as being shown in Table 1.

[0091] It was 75 ppm, when this cell carried out after [ assembly ] opening and the moisture content of the electrolytic solution in a cell can was measured. The gas chromatograph (GC-14A, Shimadzu make) performed measurement of a moisture content. In addition, the column used \*\*\*\*\* Q (1mx3phi).

[0092] When the cell assembled with the same lot was charged, there are also no phenomena, such as blistering of a cell can, and the normal cell performance was shown.

[0093] In examples 2-6 and one to example of comparison 2 example 1, except having made it the operating condition shown in Table 1, the completely same operation was performed and A size cell was made as an experiment.

[0094] Opening of the cell after each assembly was carried out, and the moisture content of the electrolytic solution in a can was surveyed. Moreover, the initial-charge examination was performed about each lot cell of this.

[0095] A result is combined and is shown in Table 1.

[0096]

[Table 1]

	電池組立 雰囲気	含浸に用 いた電解 液水分量	含浸前の 乾燥工程 の有無	電池缶内 の水分量	5 サイクル目 の電流効率	電池缶の フクレの 有無
実施例 1	RH10 % の大気中	45ppm	有	75ppm	99.6 %	無
実施例 2	RH50 % の大気中	15ppm	有	18ppm	99.8 %	無
実施例 3	RH80 % の大気中	80ppm	有	135ppm	99.3 %	無
実施例 4	RH 1 % の大気中	10ppm	無	188ppm	99.5 %	無
実施例 5	RH 1 % の大気中	250ppm	有	298ppm	98.9 %	無
実施例 6	RH50 % の大気中	250ppm	有	320ppm	98.1 %	無
比較例 1	RH50 % の大気中	250ppm	無	650ppm	97.9 %	有
比較例 2	RH50 % の大気中	15ppm	無	480ppm	98.0 %	有

Except having performed the service condition of the coating machine when manufacturing the electrode sheet of a positive electrode and a negative electrode by the coating method in seven to example 12 example 1 on the conditions shown in Table 2, the completely same operation was performed and the trial production cell was created. The binder distribution factor of a positive electrode and a negative-electrode cell sheet obtained at this time was as being shown in Table 2.

[0097] The elevated-temperature cycle examination at 60 degrees C was performed about this trial production cell. The result is combined and is shown in Table 2.

[0098]

[Table 2]

	乾 燥 条 件		バインダー分布係数		60℃サイクル試験 100サイクル目の容 量 (%)
	正極	負極	正極	負極	
実施例 7	120℃熱風	120℃熱風	1.88	1.93	92
実施例 8	60℃熱風	遠赤外線乾燥	0.96	1.18	95
実施例 9	遠赤外線乾燥	120℃熱風	0.88	1.95	93
実施例 10	150℃熱風	遠赤外線乾燥	6.8	1.05	58
実施例 11	遠赤外線乾燥	150℃熱風	0.92	5.1	49
実施例 12	25℃風乾	25℃風乾	0.41	0.38	83

In 13 to example 16 example 7, except having used the copper foil which has a surface roughness as shown in Table 3 as negative-electrode current collection field, the completely same operation was performed and the trial production cell was created. The binder distribution factor of the negative-electrode electrode sheet obtained at this time was as being shown in Table 3.

[0099] The result of the capacity retention in 60 degree-C one month retention test of the methanol immersing adhesive property test of this negative-electrode electrode sheet and a trial production cell is also collectively shown in Table 3.

[0100]

[Table 3]

	銅箔 表面粗度	負極バインダー 分布係数	メタノール浸漬 接着性テスト	60℃1ヶ月保存後の 容量保持率
実施例 13	0.6 $\mu$	1.91	5分間までブリストア発生せず。	89 %
実施例 14	0.3 $\mu$	1.95	〃	87 %
実施例 15	0.01 $\mu$	1.90	1分間までブリストア発生せず。2分間でブリストア発生。	61 %
実施例 16	0.04 $\mu$	1.91	〃	63 %

The completely same operation was performed except having used the slurry of the following composition as negative-electrode coating liquid in 17 to example 23 example 13.

[0101] As the styrene / butadiene latex 10 weight section (50 % of the weight of solid contents) created by the composition shown in Table 4 to the needle-coke trituration object 100 weight section, and a thickener, the carboxymethyl-cellulose aqueous-solution (1 % of the weight of solid contents) 100 weight section, and 1 / decanormal aqueous ammonia 1 weight section were added, and it mixed, and considered as coating liquid.

[0102] The result of the capacity retention in 60 degree-C one month retention test of the methanol immersing adhesive property test of the negative-electrode electrode sheet obtained at this time and a trial production cell is also collectively shown in Table 4.

[0103]

[Table 4]

	ラテックスモノマー組成				ゲル含量 (%)	バインダー 分布係数	メタノール浸漬 接着性テスト	60℃1ヶ月保存 性の容量保持率
	ST	BD	MMA	IA				
実施例 17	47	40	10	3	83	1.75	5分間まで ブリストー発生せず	93 %
実施例 18	42	55	0	3	80	1.81	〃	92 %
実施例 19	33	60	5	2	98	1.95	〃	95 %
実施例 20	18	80	0	2	90	1.70	〃	94 %
実施例 21	4	95	0	1	78	1.51	〃	92 %
実施例 22	47	30	20	3	55	1.78	〃	88 %
実施例 23	0	100	0	0	80	1.79	2分間で ブリストー発生	73 %

ST : スチレン

BD : ブタジエン

MMA : メチルメタクリレート

IA : イタコン酸

各々重量%組成

[0104]

[Effect of the Invention] By making Li inclusion multiple oxide into a positive active material, and setting to 5 ppm - 450 ppm the moisture content contained in the electrolytic solution in a cell can in the nonaqueous electrolyte cell which uses a carbonaceous material for a negative-electrode active material, there is also no internal pressure elevation and cell properties, such as current efficiency, can be maintained so that clearly also from the above explanation.

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[Translation done.]